Site Cooperativity Controls Glucose Isomerization and Epimerization Reactions

Scientific Achievement

Isomerization and epimerization reactions in Sn-beta were studied via first-principles simulations that accounted for the first for the role of Si-OH group adjacent to the Sn site.

Significance and Impact

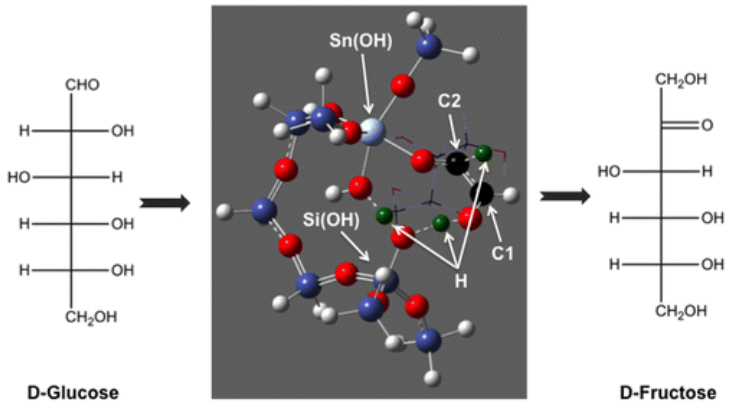
- **Isomerization and epimerization of sugars are a roadblock in converting lignocellulosic biomass to liquid fuels and chemicals.**
- **Change of solvent (H_2O vs. CH_3OH) changes the key reaction from isomerization (fructose as product; intrahydride transfer) to epimerization (mannose as product; Bilik reaction; carbon shift).**
- **Simulations reveal that the adjacent Si-OR (R=H or CH_3) controls catalyst behavior.**

Research Details

– First principles simulations on a relatively large cluster of Sn-beta zeolite were performed.

– The OH on Sn (open site) is critical for proton transfer and ring opening followed by intrahydride transfer.

– The OH on the nearby silanol (Si-OH) promotes isomerization and retards epimerization whereas its absence promotes epimerization.



3 "H" Shuttle Transition State

N. Rai, S. Caratzoulas, and D. G. Vlachos,
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